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Title: Improving the stability of organosiloxane smectic A liquid crystal random lasers using redox dopants

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Keywords: Random lasers, Smectic A liquid Crystals, Redox dopants

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Abstract: This report is focus on the development of liquid crystal (LC) visible-light scattering devices for random lasers. These light-scattering devices are based upon binary mixtures that consist of an organosiloxane smectic A LC and a wide temperature range nematogen LC. Both the temperature range of the smectic A phase and the dielectric anisotropy of the binary mixture are increased compared with that of the neat organosiloxane compound. In the latter case, the increase in the dielectric anisotropy results in a reduction of the magnitude of the electric field required to induce a clear state. Furthermore, it is found that the electric field threshold continues to decrease with increasing concentration of the nematic compound. For the random laser devices, the pyrromethene 597 laser dye was added to a mixture that was optimized for scattering and it was found that the absorption properties of the dye becomes unstable in the presence of the electro-hydrodynamic instabilities that are required to generate scattering in the LC cells. This is believed to be due to electro-chemical reactions that occur at the electrodes. To avoid dye degradation and ensure repeatable electro-optic behaviour, a reduction-oxidation (redox) couple is dispersed within the dye-doped binary mixture. It is shown that the addition of redox dopants helps to stabilize the dye in the scattering mixtures, and also increases the long-term repeatability of the scattering behaviour. Finally, we conclude by characterizing the random laser emission of the dye-doped binary mixture and demonstrate improved stability.

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We thank the reviewers' taking the time to review the manuscript and for their helpful comments. Our responses to the reviewers' comments, who have requested minor revisions, are provided below.

Reviewer #1:

Comment 1: *The paper is interesting as it reports on novel system and proposes the solution for stability improvement of similar systems, therefore it deserves publication in Optical Materials. The paper is well organized and written in good English. However, in some places minor corrections should be done: e.g. p.1, Keywords, word "Crystals" should be written as "crystals", p. 3, line 2 - in the formula defining the dielectric anisotropy a symbol "parallel" is displayed incorrectly, the same problem is on p. 3, line 4, p. 4, line 4 from the bottom, please provide the full name for CTAB (cetyltrimethylammonium bromide, or hexadecyltrimethylammonium bromide), p. 6, line 13 - Ocean Optics, p.6, line 5 from the bottom - please remove the second word "measurements", p. 11, line 10 from the bottom - the sentence "In the dynamic case…" needs correction, possibly there are some other places deserving corrections.*

Response 1: Typographical errors have now been corrected in the manuscript and the full name for CTAB has also been included. Manufacturers' details for the different experimental equipment have been included after the product name for clarification.

Comment 2: *Lettering (numbers) in figures should be enlarged and description of vertical axis in Fig. 2 b needs correction. Optical images presented in Fig. 6 have too small magnification to see the textures responsible for light scattering. In Fig. 4 c the Absorbance is not given in arbitrary units, so the bracket should be removed*

Response 2: Font and label sizes in the figures have been increased to improve clarity and, where necessary, the titles of the axes have been corrected.

Comment 3: *The role of CTAB compound, know as good surfactant, should be described in more detail, why this compound has been chosen and why its concentration has been kept constant in all the samples? How this compound influence the ordering of SmA introduced due to surface rubbing, homogenic orientation.*

Response 3: CTAB (cetyl trimethyl ammonium bromide) is an ionic compound added to facilitate electrically induced scattering in the material. It increases the ionic conductivity and allows

scattering to occur. A fixed concentration was used to ensure similarity between the samples. It is commonly added to smectic A materials for this reason [e.g. J. Phys. D. Appl. Phys. 39 (2006) 4948–4955]. In this case, CTAB is dissolved into the liquid crystal as an additive, rather than being used at the cell surfaces, and is not used for alignment purposes in the experiment. This is now explained in the manuscript (Page 5, Paragraph 1).

Comment 4: *Authors discuss the problem of dye degradation and undertake means to prohibit it but they do not show clearly how many shots are necessary to decrease the lasing efficiency to the 50% of its initial value neither for the system without redox couple nor with the redox couple.*

Response 4: Results are presented in Figure 4 on the study of dye degradation due to the application of electric fields to a 1 wt% PM597 doped mixture of (40 wt% 8/2 organosiloxane, 60 wt% BL006) + 0.1 wt% CTAB. It was found, that while the mixtures without a redox couple produce optically scattering textures that can be used for random lasing, they are not stable, and Figure 4 (c) shows the degradation in absorption after several cycles of electric fields induced switching.

It is important to be made clear here, that the dye degradation effects that are addressed in this study are electrochemically induced, and should not be confused with photo-bleaching, which is possibly what the reviewer is referring to with regards to the number the shots that will lead to observable dye degradation.

Photo bleaching of laser dyes in particular of pyrromethane (PM) dyes well described by Mula S. et.al [1]. And alternative chemical modifications have been studied to enhance the photo stability of the dyes. However, this work explains the electrochemical instability of PM dyes which is rectified by the use of redox dopants.

[1] S. Mula, A. K. Ray, M. Banerjee, T. Chaudhuri, K. Dasgupta, and S. Chattopadhyay, Design and development of a new pyrromethene dye with improved photostability and lasing efficiency: theoretical rationalization of photophysical and photochemical properties, J. Org. Chem. 73 (2008) 2146-2154.

Comment 5: *I do not understand how the response time presented in Fig. 2 c has been measured in the context of the statement that frequency of the electric field during these measurements was constant and equal 50 Hz (cf. page 7), that corresponds to 20 ms. Please explain it more clearly.*

Response 5: The rise time was measured using a triggered oscilloscope as the time interval between the 10 % and 90 % levels of light transmission of the photodiode output on the onset of switching from a scattering to a clear texture. The authors apologize for the confusion created here, where 50 Hz was the applied frequency during fall time measurements (clear to scattering), and 3 kHz was the applied frequency during the scattering rise time (scattering to clear measurements). It was a typographical error, and the 50 Hz has now been corrected to 3 KHz for rise time measurements, as 50 Hz was the frequency applied during fall time measurements. More information has been added in the text (Page 7, Paragraph 3).

Comment 6: *The electric field (E = 23 V/ micron) applied to the 8.7 micron thick LC cells was very high (i.e. voltage was around 200 V) and no electric breakdowns were observed?*

Response 6: Dielectric breakdown was not observed in these LC cells. This is consistent with previous studies that used even higher electric fields for similar materials. A sentence has been added to the text to confirm that no dielectric breakdown had been observed (Page 8, Paragraph 2).

Comments 7: *Referring to the browning of the LC mixture inside the cell and formation of bromine gas. In Fig. 6 can we see the gas bubbles in the photographs or there are simply spacers? Please comment.*

Response 7: These are the spacer beads and not gas bubbles. A sentence has been added to the captions of Figures 4 and 6 to clarify.

Comment 8: *Why Authors do not clearly show the difference in random lasing in the case of EHDI and when the field is removed. What kind of physical phenomenon is responsible for efficient light scattering when the field is absent, why the system does not return to its initial state?*

Response 8: This is actually the subject of another paper (see Journal of Applied Physics, 111, 033106, (2012)). A sentence has been added to the manuscript to refer to this study (Page 12, Paragraph 2).

Comment 9: *In Fig. 7 reporting on RL the threshold energy should be replaced by threshold energy density, as nothing is said about beam shape, radial intensity distribution or beam diameter.*

Response 9: The pump spot size has now been quoted in Figure 7 along with the beam shape so that the threshold energy density can be calculated.

Comment 10: *Judging from the spectra shown in Fig. 7 I think that Authors observe rather amplified spontaneous emission than random lasing. No sharp lines are appearing in the spectra. Did Authors average many laser shots or just present single shot responses in Fig. 7 d. ? Please comment on that.*

Response 10: The emission spectrum represents that captured over a number of shots. Although no sharp peaks are clearly observable the fact that the excitation threshold depends upon the scattering length (transport mean free path) indicates that the mechanism is random laser emission and not due to ASE. This is something that has been described previously in the literature and is often referred to as non-resonant or incoherent random laser emission.

Reviewer #2:

Comment 1: *Highlights should be rewritten according to Optical Materials standard.*

Response 1: Highlights have now been rewritten.

Comment 2: *Figure 5 should be improved.*

Response 2: The clarity of all Figures has now been improved.

Highlights

- Fabrication of light-scattering devices based on binary mixtures of smectic A and a nematic liquid crystal mixture.
- It is noticed that the increase in the dielectric anisotropy of the mixtures result in a reduction of the magnitude of the electric field required inducing a clear state.
- For the random laser devices, the pyrromethene 597 laser dye was added as a gain medium.
- To avoid dye's electrochemical degradation and ensure repeatable electro-optic behaviour, a reduction-oxidation (redox) couple is dispersed within the dye-doped binary mixture. It is shown that the addition of redox dopants helps to stabilize the dye in the scattering mixtures, and also increases the long-term repeatability of the scattering behaviour.
- This study demonstrates the random laser emission of the dye-doped binary mixture and its improved stability.

Improving the stability of organosiloxane smectic A liquid crystal random lasers using redox dopants

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Keywords: Random lasers, Smectic A liquid crystals, Redox dopants

In this paper, we focus on the development of liquid crystal (LC) visible-light scattering devices for random lasers. These light-scattering devices are based upon binary mixtures that consist of an organosiloxane smectic A LC and a wide temperature range nematogen LC. Both the temperature range of the smectic A phase and the dielectric anisotropy of the binary mixture are increased compared with that of the neat organosiloxane compound. In the latter case, the increase in the dielectric anisotropy results in a reduction of the magnitude of the electric field required to induce a clear state. Furthermore, it is found that the electric field threshold continues to decrease with increasing concentration of the nematic compound. For the random laser devices, the pyrromethene 597 laser dye was added to a mixture that was optimized for scattering and it was found that the absorption properties of the dye becomes unstable in the presence of the electro-hydrodynamic instabilities that are required to generate scattering in the LC cells. This is believed to be due to electro-chemical reactions that occur at the electrodes. To avoid dye degradation and ensure repeatable electro-optic behaviour, a reduction-oxidation (redox) couple is dispersed within the dye-doped binary mixture. It is shown that the addition of redox dopants helps to stabilize the dye in the scattering mixtures, and also increases the long-term repeatability of the scattering behaviour. Finally, we conclude by characterizing the random laser emission of the dye-doped binary mixture and demonstrate improved stability.

1. Introduction

Liquid crystal (LC) light scattering devices have been an area of keen interest for more than three decades[1], both from an application and theoretical viewpoint[2], [3]. One of the main applications associated with LC-based scattering devices has been the commercial realization of 'smart' windows[4][5], whereby the window can be switched between scattering (opaque) and transparent states using electric fields. Moreover, in addition to applications that make use of macroscopic light scattering such as 'smart' windows, display devices, and optical storage components[6], [7], highly scattering LC compounds have applications that utilize the microscopic disorder as well. For example, applications such as random lasers harness the inherent local disorder in the refractive indices in order to achieve optical feedback through the multiple scattering of light[8].

Early LC scattering devices made use of polymer-dispersed LCs for the purposes of smart windows [9]–[12], but these devices had inherent problems that hindered their widespread commercial use, such as including the need for a continuous application of an electric field to maintain a clear transparent state [13]. As an alternative to polymer-dispersed LCs, devices based upon the electro-hydrodynamic instabilities (EHDI) in Smectic A (SmA) LCs were proposed and demonstrated[14]. The significant advantage of SmA based devices is that they are bi-stable (i.e. they exhibit two stable states in the absence of an electric field), eliminating the need for a continuous application of an electric field. It was shown by Gardiner et al. [14][15] that organosiloxanes represent a very promising type of low-molar mass materials for such scattering devices. Organosiloxanes possess a high negative conductivity anisotropy[6], while also exhibiting a SmA phase across wider temperature ranges than that observed previously for the corresponding chain length alkyloxy-cyanobiphenyl LCs [7]

The two zero-field stable states are referred to in this paper as the 'clear' and 'scattering' states; either can be accessed with the application of a suitable voltage amplitude and frequency. Understanding the material parameters that underpin the dynamic light scattering behaviour in SmALCs is important in order to develop devices with lower driving threshold voltages. Theoretical studies into the dynamic scattering behaviour of SmA LCs were performed by Guerst and Goosens [2], who based their model on the continuum theory [16]. The scattering and

clear threshold electric field magnitudes are then given as

$$V_{\text{scattering}} \propto \frac{d}{\varepsilon_{\parallel}\left(1-\frac{\sigma_{\parallel}}{\sigma_{\perp}}\right)} \quad (1)$$

$$V_{\text{clear}} \propto \frac{d}{\Delta\varepsilon} \quad (2)$$

respectively, where *d* is the thickness of the LC material sandwiched between two electrodes, Δε is the dielectric anisotropy (Δε = $\varepsilon_{\parallel} - \varepsilon_{\perp}$), and $\sigma_{\parallel}/\sigma_{\perp}$ is the ratio of the conductivities parallel and perpendicular to the molecular long-axis. It is clear that the low parallel conductivity $\sigma_{\parallel}$ of organosiloxane LCs [6] and relatively high values of $\sigma_{\perp}$ are beneficial for low scattering threshold voltages. However, the low values of the dielectric anisotropy Δε and parallel dielectric constant $\varepsilon_{\parallel}$, typically lead to higher clear threshold voltages.

In order to enhance the scattering properties, conventionally, ionic compounds have been added to SmA LC mixtures [14], although this can dramatically reduce the lifetime of the subsequent device [17]. This limitation on the lifetime is thought to be the result of a decomposition of the ionic components due to electrochemical reactions at the electrodes (Indium Tin Oxide, ITO), leading to a gradual loss of conductivity and thereby limiting the long term functionality of the devices. It was proposed in a previous study that, for LC mixtures consisting of ionic dopants, the application of electric fields at kHz frequencies can extend the device lifetime by minimizing the ionic purification that is otherwise aggravated when using electric fields at low frequencies [17]. Furthermore, while other scattering devices such as random lasers based upon dye-doped SmA LCs have already been demonstrated, the effect on the photo-luminescent properties of the dye due to the ionic dopants is currently unclear [18][19].

The purpose of this paper is to demonstrate that, through the use of binary mixtures that combine an organosiloxane LC with a wide temperature range nematogen LC, it is possible to fine-tune the material parameters in an attempt to reduce the threshold voltages, decrease response times, and increase the SmA phase range leading to light scattering devices with improved electro-optic characteristics. We then dope these optimised mixtures with a high quantum efficiency laser dye to create a random laser device. It is observed that repeated cycling

of the frequency or amplitude of the applied electric field can result in a degradation of the absorption and consequently emission properties of the dyes. Even though random lasers using dye-doped SmA LCs have been demonstrated previously [18][19], there has been no comment on the degradation of the dye. To address the issue of lifetime, we show that with the addition of a reduction-oxidation (redox) couple it is possible to improve the repeatability of the scattering characteristics leading to a substantial increase in the dye stability.

The manuscript is organised as follows. To begin with, the materials used in this study are introduced in Section 2 followed by the experimental details in Section 3. Results and Discussion are presented in Section 4.

2. Materials

Organosiloxanes can be considered to possess three distinct units in the molecule. These molecules consist of an aliphatic chain, an aromatic core (ringed hydrocarbons), and a siloxane (Si-O-Si) group at one end. An illustration of an A/2 organosiloxane, where A represents the number of carbon atoms in the aliphatic chain and 2 represents the number of siloxane units is shown in Figure 1 (a). The initial interest in these materials was sparked by the search for low molar mass materials for fast electro-optic switching applications as a substitute to polymeric LCs [7].

Organosiloxanes typically have high negative conductivity anisotropies and a conductivity ratio (parallel to perpendicular conductivity) as low as 0.011, which was reported for the 8/2 compound [15]. In addition, organosiloxanes generally have low dielectric anisotropies which means that relatively large electric fields are required to obtain a clear transparent state [14]. A previous study found that the threshold could be lowered slightly by doping with a monomesogen with a higher dielectric anisotropy. In attempt to lower the electric field threshold, we have prepared binary mixtures consisting of the 8/2 organosiloxane compound with the nematogen mixture BL006 (MERCK KGaA, $\Delta\varepsilon \sim 17$). To determine the optimum concentration of BL006 in the 8/2 compound, five mixtures were prepared. The compositions of the mixtures are shown in Table 1.

To induce scattering textures with the application of electric fields in the binary mixtures an ionic dopant, 0.1 wt% cetyltrimethylammonium bromide (CTAB) has also been added to all of the test materials. CTAB is an ionic compound added to facilitate electrically-induced scattering in the material. It increases the ionic conductivity of the mixture and enables light scattering to occur and it is commonly added to smectic A LCs for this reason [14, 17]. A fixed concentration was used to ensure similarity between the samples. In this case, CTAB is dissolved into the LC as an additive, rather than being implemented at the cell surfaces, and is not used for alignment purposes in this experiment. Similar doping has also been done in previous studies [15][6] where it has been shown to contribute towards the generation of EHDI through ionic flow perpendicular to the layers in the SmA that are induced by the application of electric fields.

After the initial material and electro-optic characterization, the mixtures were doped with a laser dye Pyrromethene 597 (Exciton, PM 597). The molecular structure of the dye molecule is shown in Figure 1 (b). The laser dye was added at a concentration of 1 wt% into the binary mixtures. PM597 has been reported to have high solubility in LC hosts and a previous study on the comparisons of commercial laser dyes in LC hosts for band-edge lasing reported that PM597 exhibits a high quantum efficiency and relatively low laser excitation thresholds (optical pump power) in chiral nematic LC lasers. A reduction-oxidation couple was also added to the LC medium in order to increase dye-stability and lifetime of the device. Specifically, these are TCNQ (tetracyanoquinodimethane), which serves as an electron-acceptor, and PDA (*p*-phenylenediamine), which serves as an electron donor, were used as redox dopants. The molecular structures of the respective dopants are illustrated in Figures 1 (c) and (d).

3. Experimental techniques

For the majority of the measurements, the LC mixtures were capillary filled into 8.7 µm-thick glass cells (Instec). The cells consisted of glass substrates coated with ITO electrodes and anti-parallel rubbed polyimide alignment layers. The LC was sandwiched between the two glass substrates that were separated by spacers and glued together.

An Olympus BH-2 polarizing microscope was used to characterise the samples. The

microscope was used with inter-changeable outputs, including a camera to record optical micrographs (PixeLINK), a photodiode (PDA55, Thorlabs) to quantify transmitted intensity through the scattering cells, and a spectrometer (USB-2000, Ocean Optics) that was used to record the absorption and transmission spectra of dye-doped mixtures. For mesophase identification during phase transition temperature measurements, the microscope was placed in a crossed polarizers arrangement, whereas for light scattering studies a parallel polarization configuration was used. For phase transition temperature measurements a heating stage connected to a precision temperature controller (TMS 94, Linkam) was used. Accurate phase transition temperature measurements were also performed using differential scanning calorimetry (DSC) on a calorimeter from Mettler Toledo (823^e).

To study the light scattering characteristics and its frequency dependence, a function generator (TG1304, TTi) was used in combination with a high voltage amplifier (built in-house) and the output was applied to the test cells, placed on the microscope hot-stage. A photo-diode was used to quantify the light transmission and the output was fed to the digital oscilloscope (DSO5034A, Agilent Technologies). To quantify light scattering, the same initial reference light intensity was used for all the samples, and the results were normalized with respect to the fixed reference for an accurate comparison. This set-up was also used to measure the 10-90% (scattering to clear state) response times. All electro-optic measurements were performed at a temperature of 25°C.

Dielectric and conductivity anisotropy measurements of test cells were performed using an LCR component analyser (6440A, Wayne Kerr). The component analyzer meter was used to perform frequency sweeps to record the cell characteristics as a function of applied frequency. For the random laser characterizations, the LC cells were optically pumped by a pulsed (4 ns), Q-Switched, frequency doubled (λ = 532 nm) Nd-YAG laser, (Polaris II, New Wave Research). The output light was coupled from a fibre into an ocean optics HR-2000 spectrometer with 0.3 nm-resolution.

4. Experimental Results

In order to determine the variation in phase transition temperatures for the various mixture compositions, phase transition measurements were performed using a DSC, whereby DSC traces were then correlated with phase identification using polarizing optical microscopy. The DSC

results are summarized in Table 2. It can be seen that there are bi-phasic regions, 2-3°C wide, which are a known characteristic of organosiloxanes and are not believed to be due to a lack of sample purity. It is clear that increasing the concentration of the nematogen mixture results in an increase in the transition temperature of the SmA phase, while also lowering the crystallization temperature thereby widening the temperature range of the SmA phase. It should be noted however, that the 80 wt% mixture no longer exhibits a SmA phase so in this study useful SmA based devices can only be made up until a 60 wt% concentration of the nematogen mixture.

Measurements of the dielectric anisotropy measurements, illustrated in Figure 2 (a), show that increasing the concentration of the nematogen mixture results in an increase in the dielectric anisotropy. This is a highly desirable result as the 1% CTAB doped 60 wt% BL006, 40% 8/2 organosiloxane mixture has a dielectric anisotropy of $\Delta\varepsilon = 4.8$ and still exhibits a SmA phase. Conductivity anisotropy results are summarized in Figure 2(b), where they are presented as a ratio of the conductivities parallel and perpendicular to the director. It can be seen that the ratio is always less than unity, leading to negative conductivity anisotropy. Furthermore, it is clear that in the 40% and 60% nematogen mixtures there is a significant improvement in the dielectric anisotropy, while still maintaining the high negative conductivity anisotropy of the constituent organosiloxanes. In accordance with Eqs. (1) and (2), these results are very desirable for making electro-optic devices with lower scattering and clear threshold voltages.

The response times required to generate the scattering and clear states were found to vary for the different mixtures. The switching time is taken to be the time interval between the 10 % and 90 % intervals of the respective change in light transmission. The rise time is defined to be the time taken for the LC cells to switch from a scattering texture to a clear texture (induced by applying a high applied electric field frequency 3 KHz), whereas the fall time represents the reverse case (induced at a low applied frequency, 50 Hz). Figure 2(c) demonstrates the rise and fall times for one specific mixture, (40 wt% organosiloxane + 60 wt% nematic) where it can be seen that as the electric field magnitude increases, the response time decreases. The change is quite dramatic and we note that the rise time (scattering to clear) decreases from 200 ms to 6 ms as the field magnitude is increased from $E = 7.5$ V/µm to $E = 15$ V/µm, at a fixed frequency of $f = 50$ Hz. Figure 2(d), on the other hand, illustrates a comparison of the switching times across

the binary mixtures. It can be seen that having a higher concentration of the organosiloxane compound favours a faster clear-to-scattering (fall time) transition, whereas a higher concentration of the nematogen mixture favours a faster scatter-to-clear (rise time) transition. The improvement in the fall time can be explained with reference to the EHDI scattering in the SmA phase, which is generally dominated by the conductivity anisotropy [6], so it might be expected that a higher concentration of the organosiloxane would favour this state. On the other hand, the scattering-to-clear transition is related to the dielectric anisotropy and, therefore, mixtures with a higher concentration of the nematogen exhibit faster rise times, which correlates with the dielectric anisotropy trend in Figure 2(a).

To compare the light scattering behaviour of the five mixtures, measurements of the transmission as a function of the applied frequency were performed on all the mixtures at different applied electric field magnitudes. An example of these measurements at two different applied E-field magnitudes of E = 19 V/µm and E = 23 V/µm are summarized in Figure 3(a) and Figure 3(b), respectively (it should be noted that no dielectric breakdown was observed for these electric field strengths). At low applied frequencies, it can be seen that the transmission is relatively low and most of the light incident on the cell is scattered by the sample. The reason for the observed effect is that at low applied frequencies the ionic motion of the CTAB molecules dominates and their motion distorts the microscopic texture of the medium, resulting in the formation of micron-sized scattering domains. However, on increasing the applied frequency of the electric field, it can be seen that there is a change in the observed texture, which results in a clear state. This effect takes place when the applied frequency is high enough to overcome the motion of the charge carriers, allowing for dielectric reorientation of the molecules, which then results in a clear transparent appearance between crossed polarisers (since the dielectric anisotropy is positive)[8]. From these figures, it is evident that the mixtures exhibit different electric field thresholds for the scattering-to-clear transition. Overall, it was determined that the mixture with the lowest electric field threshold was Mix 3 (40 wt% SmA, 60 wt% N), since it had a higher concentration of the nematogen mixture and correspondingly higher dielectric anisotropy, but still exhibited a SmA phase.

Having established the optimum mixture in terms of electric field thresholds and response

times, we then dispersed a low concentration of laser dye (1 wt% PM597) in to Mix 3 (40 wt% 8/2 organosiloxane, 60 wt% BL006, Nematic) + 0.1 wt% CTAB). To begin with, we carried out experiments to check the lifetime and stability of the dye-doped LC mixture, the LC cell was cooled to room temperature from the isotropic phase and then subjected to 10 consecutive cycles at an electric field magnitude of E = 12 V/μm, with frequencies applied from f = 30 Hz – 1500 Hz, in steps of 20 Hz. As can be seen from Figure 4(a), there is a significant variation in the transmission-frequency characteristics with time; evident from the decrease in the transition frequency (transition frequency between the scattering and clear states). This corresponds to a continuous reduction in the opacity of the scattering state of the cell at higher frequencies due to the restoring dielectric torques aligning the molecules homeotropically (inducing the clear state) at lower frequencies. It can also be seen that the response saturates, such that the change in transition frequency between the 1st and 2nd cycle is about 250 Hz, whereas the change between the 2nd and 3rd cycle is only approximately 100 Hz. Moreover, this change reduces considerably for the 9th to 10th cycle.

The shift in the transmission as a function of frequency with repeated cycling is considered to be due to a change in the conductivity, which is thought to be a manifestation of electrolytic purification [17]. In turn, this is caused by electro-chemical reactions that occur inside the cell, due to the formation of stable neutral molecules at the cell electrodes. Figure 4 (b) illustrates changes in the conductivity of the LC cell for repeated cycles and shows a sharp decrease after the 1st cycle followed by a more gradual yet persistent decrease. A similar problem was encountered during earlier work on electro-optic characteristics of organosiloxanes [15]. It was proposed that this is the result of the formation of bromine gas Br_2, due to the reaction of the bromide Br^- ions (present due to CTAB doping) at the electrodes. Evidence to support this claim is the noticeable browning of the LC mixture inside the cell, hinting towards the formation of bromine gas. In previous works, it was suggested that the electro-chemical degradation was much lower at higher frequencies (e.g. f > 100 Hz), for which the lifetimes of bistable organosiloxane scattering devices were greater than 24 hours. At f = 10 Hz, the lifetime was reduced to only 40 minutes, which is further evidence that the degradation effect is electro-chemical in nature. However, in our study, even the application of higher frequency (f > 100 Hz) electric fields resulted in a rapid loss of conductivity. This could be due to the fact that the scattering mixture also contains dye molecules, which were not present in previous studies.

In addition to the alteration in the electro-optic properties with repeated cycles of the applied frequency, a second and more severe problem is that of dye degradation. For the dye-doped mixture that was subjected to ten sweeps of the frequency (Figure 4 (a)), post experiment absorption spectra were recorded and the results are given in Figure 4 (c). It should be noted here that the spectra were taken in the isotropic phase, to rule out any effects of alignment of the dye by the LC host. To determine if degradation effects are seen with only PM597 or whether it is a more general phenomenon that affects the stability of organic dyes, similar trials were performed with other organic laser dyes such as DCM and LD800 and similar degradation effects were recorded.

The stark contrast between absorption inside and outside the electrode region is illustrated by the optical micrographs shown in Figure 4 (d). In combination with the spectrum in Figure 4 (c), the results suggest that there have been electrochemical reactions in the regions where the electric field was applied, thus affecting the absorption characteristics of the PM597 dye. This is a significant problem, as it would affect the lifetime and stability of any random laser or dye-doped smart windows that will be made from these scattering mixtures. It is clear from Figure 4(d) that there is a loss of pigmentation in the electrode region. A possible explanation for the observed degradation is that the degree of electronic conjugation in the dye molecules is reduced as a result of a reduction in the electrochemical cell by the Br^- ion released into the mixtures by the CTAB, resulting in a change in dye absorption characteristics. This explanation is plausible as the degradation was found to be partially reversible after several days of no exposure to electric fields. The reduction of the PM597 molecules is a reversible reaction and it is possible that over time the dye molecules lose the excess electrons gained at the electrodes thereby reversing the observed dye degradation. However, detailed electrochemical studies are required to analyse all the intermediate chemical species present in the electro-chemical environment of the cell in order to obtain a better understanding of the degradation in the dye characteristics.

Nevertheless, in an attempt to circumvent the issue of dye degradation, we decided to add reduction – oxidation (redox) molecules to the mixture. It was postulated that the addition of reversible oxidative and reductive molecules could potentially protect the dye from destructive reduction, while also maintaining ionic circulation to enable EHDI scattering. Redox dopants

form reversible charge transfer complexes that enable scattering, while at the same time they are not consumed in the process. To test whether redox dopants help minimize the dye degradation issues and also improve the stability and repeatability of the TF characteristics, the 8/2 Organosiloxane + BL006 + 0.1 wt. % CTAB + 1 % PM 597 dye mixture was doped with the redox dopants TCNQ and PDA, where TCNQ is employed as an electron acceptor and PDA as an electron donor.

Results for the transmission versus frequency sweeps and the dye stability are summarized in Figure 5(a) and (b). In Figure 5(a), it is clear that the cycle-to-cycle variation in the transmission frequency characteristics are greatly improved with the addition of the redox dopants. However, perhaps an even more notable result is the enhanced stability of the dye molecules in the scattering environment, which is of importance for the random lasers. It can be seen from the absorption spectrum in Figure 5(b) that there is almost no observed dye degradation in the cell, even after the repeated cycles. This is a key result, and shows that the addition of the redox dopants to the mixture has also aided in stabilizing the dye in the dynamic scattering state preventing reduction. Redox dopants have been added to ionic-doped LCs previously [20] and they were also found to increase lifetime of scattering devices based upon nematic LCs.

An illustration of the light scattering characteristics as seen under a POM for an optimized mixture (Mix5, 0.5% PDA, 0.5 % TCNQ, 1 % PM 597, 0.1 % CTAB doped 40 % 8/2 SmA, 60 % BL006 N) is shown in Figure 6. It is clear that the change in texture as a function of applied electric field is very dramatic. The scattering textures are stable after the removal of the applied electric field and the control of the scattering texture by the applied electric-field frequency allows the tuning of the scattering mean free path of light within the medium. This allows dynamic control of the amount of scattering and would open up several exciting applications that can make use of the electrically switchable dye-doped scattering textures.

By optically pumping the dye-doped mixture with the second harmonic of an Nd:YAG laser, random lasing was observed. For these experiments, 20 µm-thick glass cells were capillary filled and random lasing was investigated as a function of the applied electric field frequency at a constant electric field magnitude of E= 12 V/µm. A variation of the full-width at half maximum

(FWHM) with applied frequency for Mix5 is shown in Figures 7 (a) and (b), where it can be seen that for low frequencies there is a characteristic sigmoid profile. For random lasers, the sharp decrease in FWHM corresponds to the excitation energy threshold [21], [22]. At high frequencies (e.g. f = 670 Hz), as can be seen in Figure 7(b), there is no longer any narrowing, since the texture switches into a clear state and there is not sufficient scattering to induce random lasing. This corresponds directly to both the optical micrographs shown in Figure 6 and the frequency dependent transmission characteristics shown in Figure 5, demonstrating the tunable aspect of the devices.

Figure 7(c) illustrates the variation in lasing threshold as a function of applied electric field frequency. It is clear, that changing the applied frequency allows us to change both the spectral FWHM and the excitation energy threshold of the random lasers. In addition, it can also be seen that these laser devices can be operated under two driving schemes, that we refer to here as the 'dynamic' (continuously applied electric field leading to EHDI and consequently dynamic scattering) and 'static' (electric field is removed but a scattering state is preserved because of the bistable nature of the materials: local inhomogeneities in the refractive indices are present that lead to light scattering) conditions. A previous study [19] has considered the difference in excitation threshold for the dynamic and static cases whereby the laser threshold was found to be lower in the dynamic case (continuously applied electric field case), as the turbulent motion of the LC medium (EHDI) in the cell is enhancing the amount of optical disorder, effectively forming a better cavity with a smaller scattering length and lower pump thresholds. The spectral profile as a function of increasing pump pulse energy is shown in Figure 7 (d), and the relative narrowing of the emission spectrum centred on the dye emission maximum of 580 nm can be seen.

4 Conclusion

It has been demonstrated that binary mixtures of 8/2 Organosiloxane SmA and a nematogen BL006 show improved electro-optic and mesophase characteristics compared with the neat organosiloxane materials for light scattering applications. The results indicate that the binary mixtures increase the temperature range of the SmA phase (up to a concentration of 60 wt% of the nematogen). At the same time the dielectric anisotropy is increased by a factor of 12 over the

neat organosiloxane material, resulting in lower driving voltages. Adding dye to the light scattering mixtures resulted in issues with the repeatability of the switching that manifest as a loss of dye absorption accompanied by large hysteresis in the transmission-frequency response. In order to improve the stability we added the redox dopants TCNQ and PDA, and it was demonstrated that dye stability and repeatability of the scattering behaviour improved. The redox-stabilized medium facilitates the long term operation of the dye-doped electro-optic light scattering devices and stable random lasing from one of the stabilized redox-doped mixtures was demonstrated.

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Table Captions

Table 1. Compositions of the base mixtures. All concentrations are given as percentages by weight.

Table 2. Phase transition temperatures of the different mixtures, measured using differential scanning calorimetry. Cr: Crystalline, I: Isotropic.

Figure Captions

Figure 1 (a) A/2 Organosiloxane molecular structure. A = 8 for 8/2 used in this research. (b) Chemical structure of the Pyrromethene 597 dye molecule. (c) Chemical structure of TCNQ (electron acceptor) and (d) PDA (electron donor) molecules.

Figure 2 (a) Dielectric anisotropy as a function of concentration of the nematogen. These measurements are at *f* = 10 KHz. (b) Variation in conductivity anisotropy (*f* = 100Hz) with increasing nematic concentration.. (c) Rise time (scattering – clear) and fall time (clear – scattering) as a function of the electric field magnitude for the 40 % 8/2 SmA, 60 % BL006 N-LC mixture. (d) Rise time and fall time as a function of the concentration of the nematogen (field magnitude applied was the minimum threshold electric field for each respective mixture).

Figure 3 Transmission-frequency curves at an applied electric field of (a) E = 19 V/µm and (b) 23 V/ µm for a (40% SmA, 60 % N, 0.1 % CTAB) binary LC mixture.

Figure 4 (a) Transmission-frequency (TF) characteristics for 10 consecutive cycles at an applied electric field of E = 12 V/µm. (b) Variation of the conductivity (uS/m) and capacitance (pF) across consecutive TF runs. (c) Absorption spectrum of the cell after the TF runs. Two curves are shown, inside (—) and outside (—) the electrodes. Spectra recorded in the isotropic phase, T = 100 °C. (d) Optical micrographs of the texture seen in the isotropic phase inside (left) and outside (right) of the electrodes, illustrating the change in the dye absorption characteristics. Results shown for 1 wt % PM597 doped mixture of (40 wt% 8/2 organosiloxane, 60 wt% BL006) + 0.1 wt% CTAB, cell thickness 8.7µm; T = 25°C. Spacer beads can also been seen.

Figure 5 (a) Transmission frequency characteristics with the addition of 1 wt% (0.5 % PDA, 0.5 % TCNQ) redox dopants in Mix 3 (40% SmA, 60 % N, 0.1 % CTAB), at 12V/µm. (b) Absorption spectra of the redox-stabilised dye doped mixtures ; inside (—) and outside (—) the regions of the electrodes after the TF runs.

Figure 6 Optical micrographs illustrating the textures seen under the microscope for Mix 3 (40%SmA, 60%N). (a) Initial texture at room temperature, cooled from the isotropic phase. (b)

E=12V/µm, 70 Hz strong scattering. (c) E=12V/µm, 350 Hz, scattering (d) E = 12V/µm, 3 KHz, Clear stat. The cell thickness was 8.7µm. Spacer beads can also been seen.

Figure 7 Random Laser results. FWHM as a function of excitation pulse energy for the dynamic scattering state for different applied electric field frequencies (12 v/ µm). (a) corresponds to frequencies between 70 Hz – 250 Hz whereas (b) corresponds to high frequencies. (c) Variation of the pump laser pulse energy at lasing threshold as a function of applied frequency for the 'dynamic' (—) and 'static' (—) scattering cases, where 'dynamic' refers to the case where electric fields are applied continuously, and 'static' refers to the case where the electric field is removed after inducing a scattering texture of the respective frequency/magnitude . (d) Spectral profile of the random laser emission as a function of different magnitude of pump pulse energy. The pump beam exhibited a near-Gaussian intensity profile and the pump spot diameter was 100 µm.

Mixture Name	Composition
Mix 0	100 % 8/2 Organosiloxane + 0.1 % CTAB
Mix 1	80 % 8/2 + 20 % BL006, + 0.1 % CTAB
Mix 2	60 % 8/2 + 40 % BL006, + 0.1 % CTAB
Mix 3	40 % 8/2 + 60 % BL006, + 0.1 % CTAB
Mix 4	20 % 8/2 + 80 % BL006, + 0.1 % CTAB

Table 1

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Optical Materials

Mixture (% weight)	Phase Transitions on heating (°C)
Mix 0	(Cr-SmA) 44.2 (SmA – I) 64.3
Mix 1	Biphasic (SmA, I) : 70 – 72 Clearing Point (SmA – I) : 72.5
Mix 2	Biphasic (SmA, I) 71.5 – 75.4 Clearing Point : 75.5
Mix 3	Multiphasic (SmA, N, I): 75.1 – 84.9 Clearing point : 85
Mix 4	Clearing point (N - I) : 91.3

Table 2

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Optical Materials

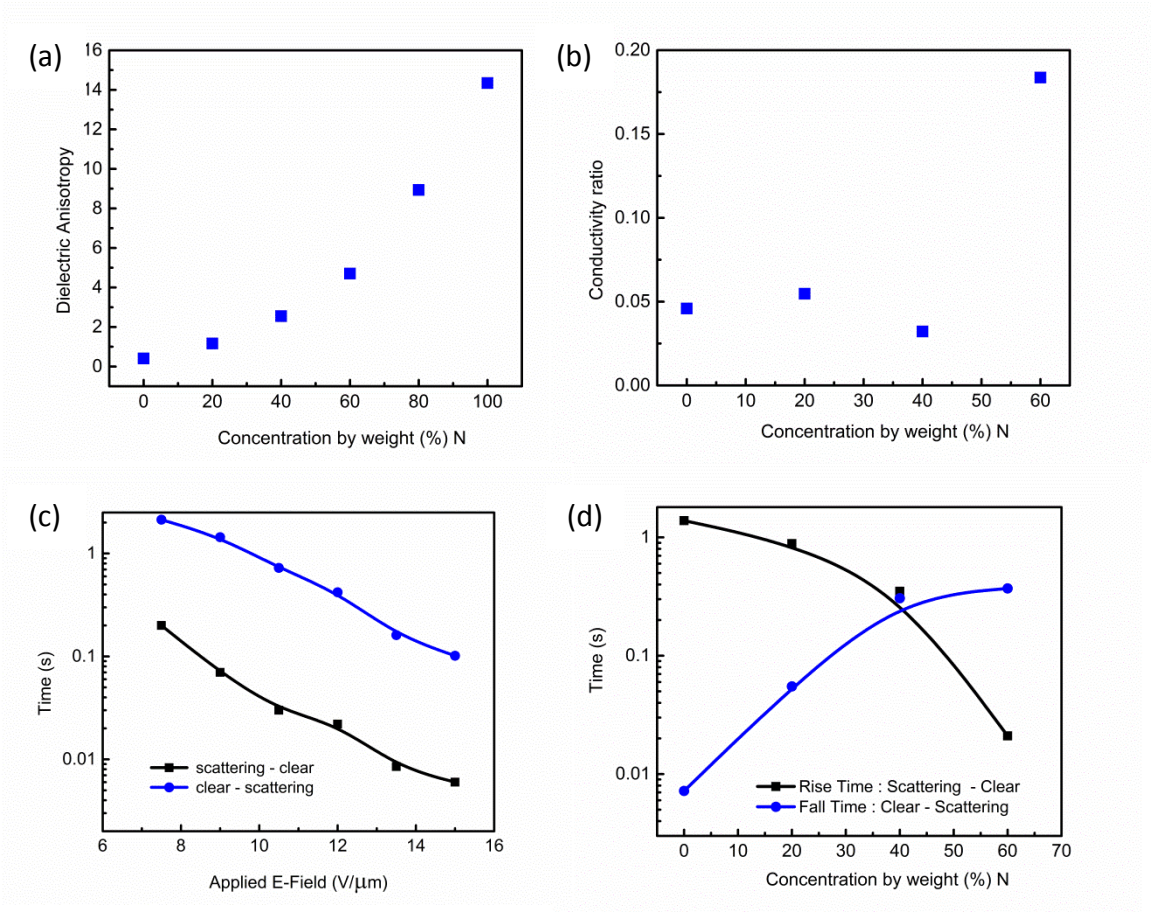

Figure 2

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Optical Materials

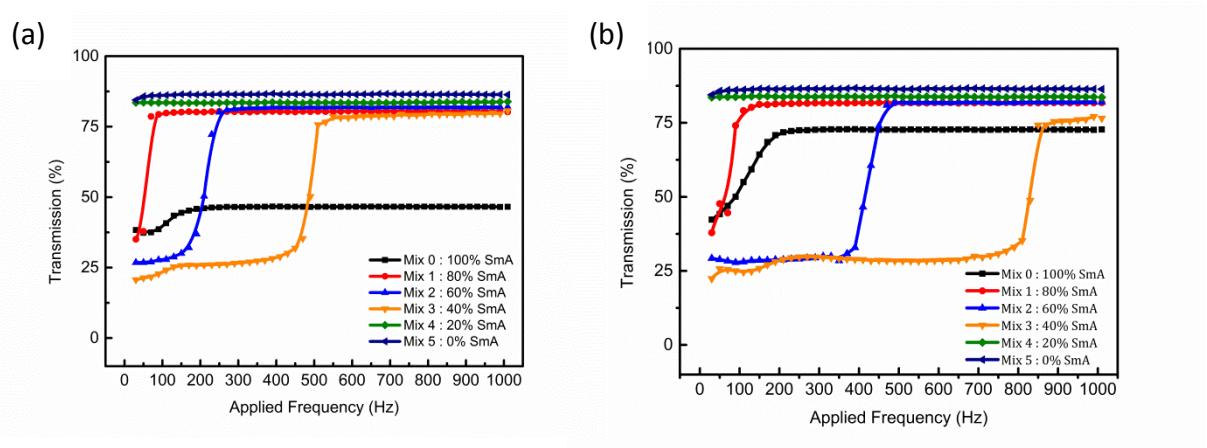

Figure 3

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Optical Materials

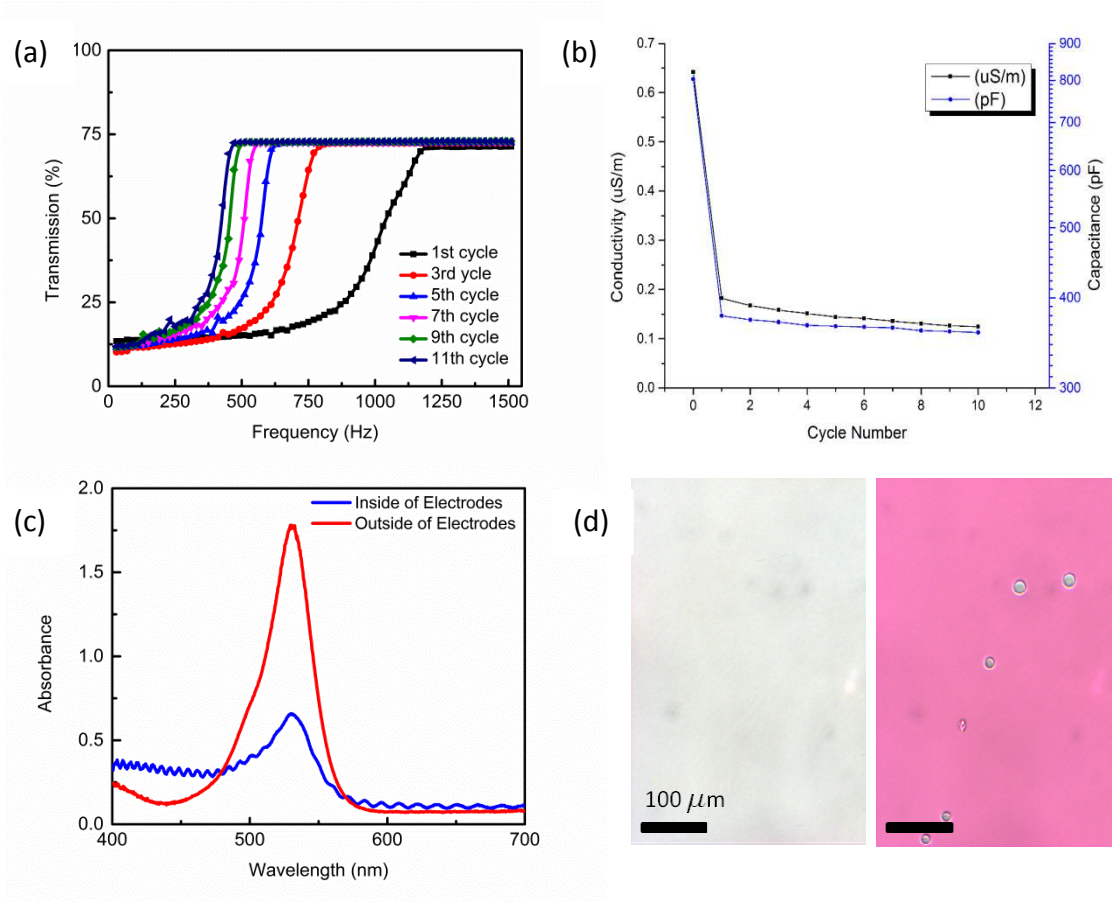

Figure 4

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Optical Materials

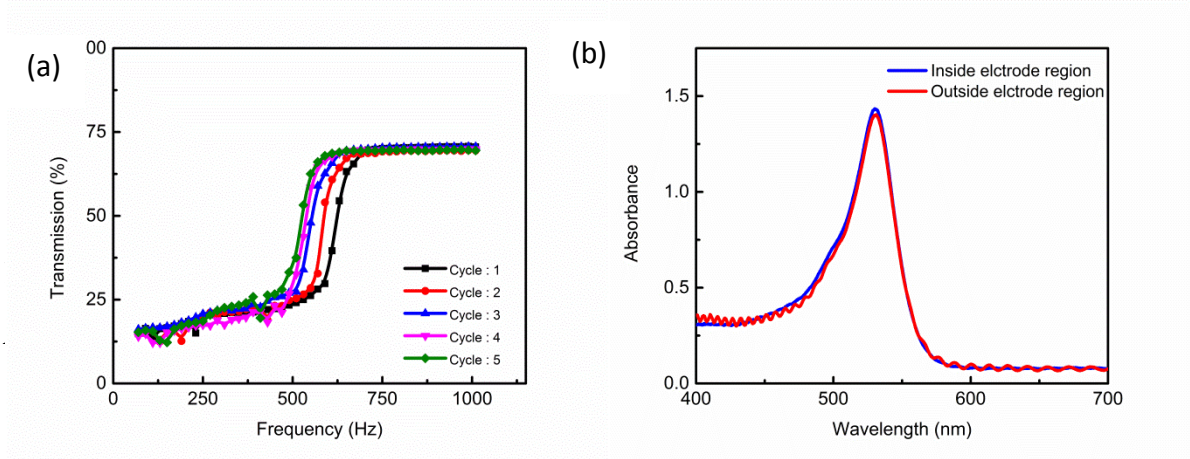

Figure 5

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Optical Materials

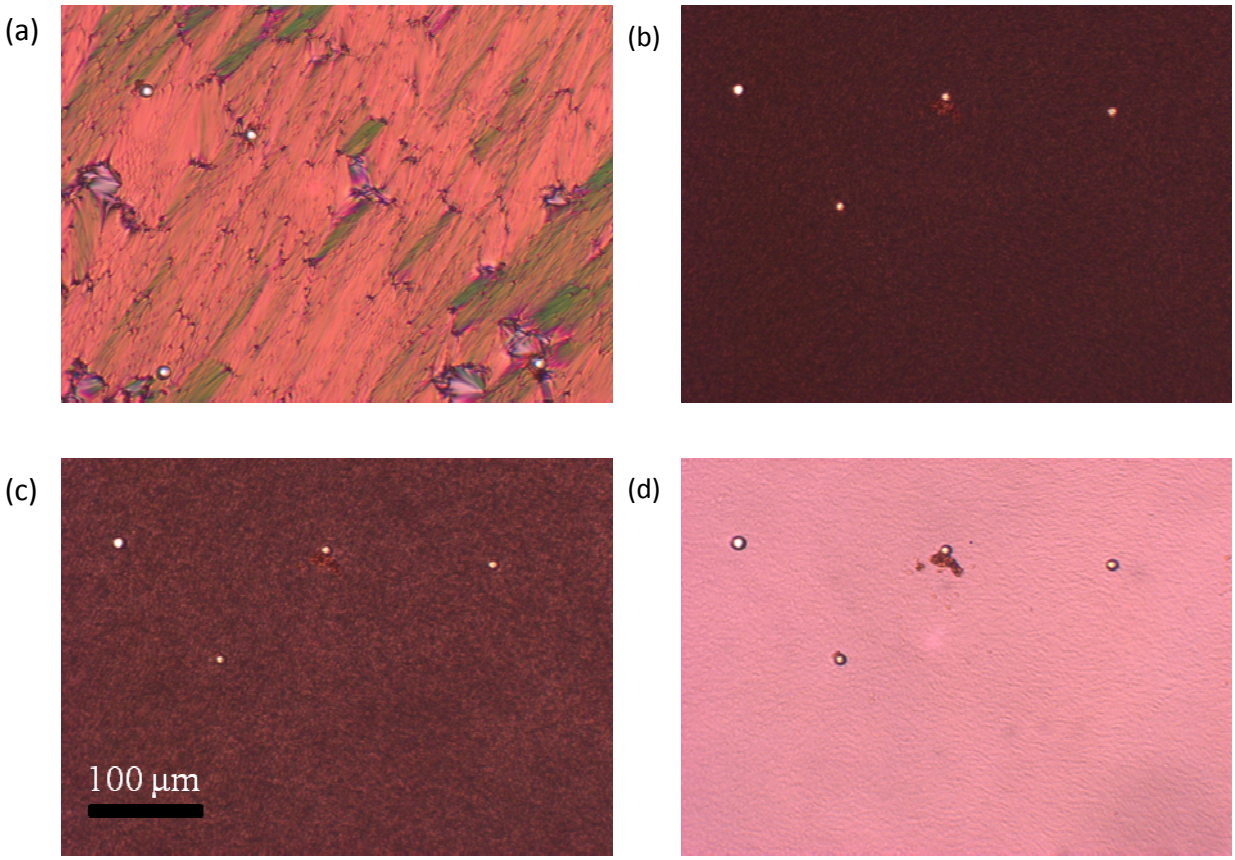

Figure 6

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Optical Materials

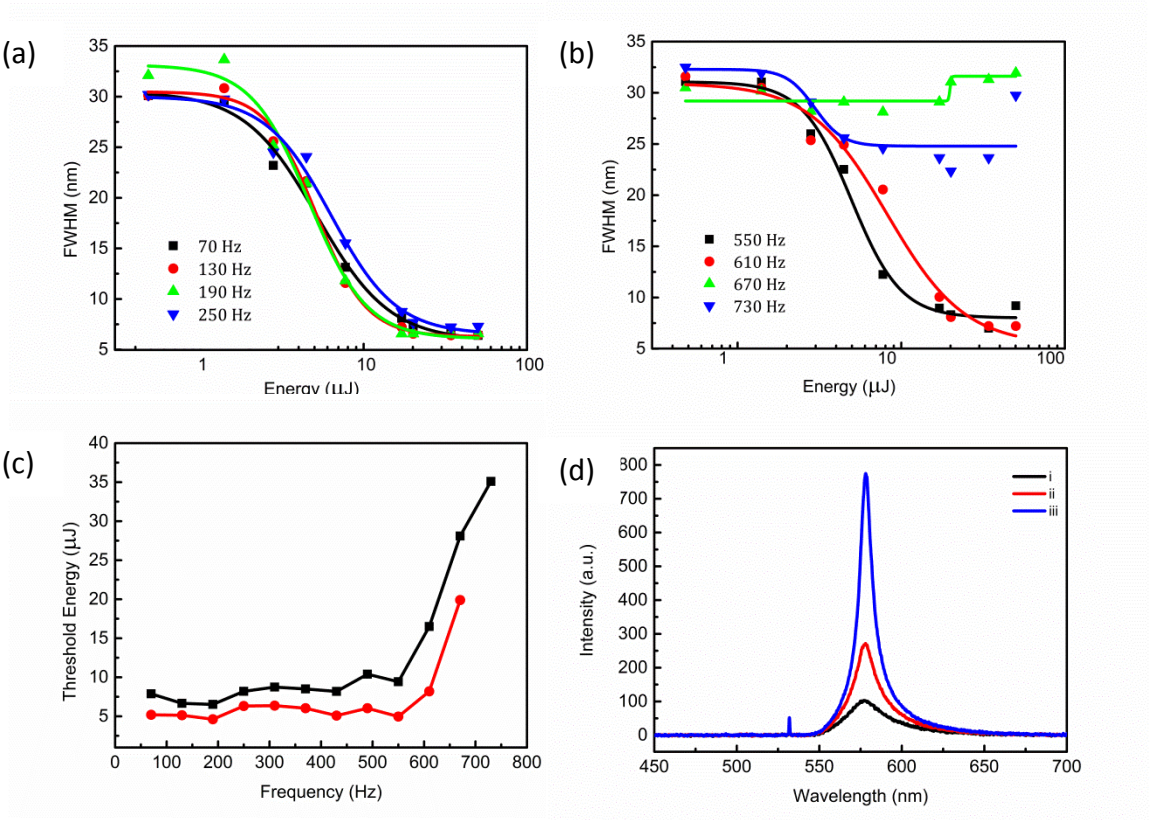

Figure 7

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Optical Materials